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Report
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Solutions with new Chemical
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Formation of continuous solid solutions with new chemical Compounds.

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Abstract

The brief review of experimental data on semiconductor continuous solid solutions with new chemical compounds is given. The Solubility in the multicomponent solution-melt is discussed. Conditions of the formation of the continuous substitutional solid solutions with covalent as well as metal bonds are substantiated. In the context of mutual solubility increase the following extended conception is suggested. In the multicomponent systems the formation of the continuous liquid or solid solutions is possible as a result of origination and dissolution of new chemical compounds, which are not shown on the traditional phase diagrams. The existence of many continuous solutions based on molecular elements, IV-IV, III-V, II-VI and I-VII type binary compounds is predicted. Four versions on the formation of the molecule of new chemical compounds in liquid - crystal phase transition are considered. As an example the possibility of the synthesis of some continuous solid solutions based on the aluminum is discussed.

Introduction

There exist a great variety of solutions ranging from molecular ones to microemulsions with the size of particles of 100\AA . One of the basic properties of the solution is the solubility, which expresses the concentration when phase is saturated by the component and phase transformation takes place. Because of the absence of the quantitative theory of the solubility in multicomponent systems to develop the advanced technologies some ideas on the formation of new concentrated solutions is needed. Progress in the growth of semiconductor layers by chemical vapor deposition and liquid phase epitaxy made it possible to obtain $(\text{IV}_2)_x (\text{III-V})_{1-x}$ type continuous solid solutions concerning Ge-GaAs, Ge-GaSb, Si-GaAs, Si-GaP and Ge-InP systems. On the basis of these data and considering IV_2 (Ge_2 , Si_2) as a new chemical compound we have suggested the conception, according to which the formation of the continuous substitutional solid solution is a cause for origination of new chemical compounds not shown on the traditional phase diagrams [1].

In this paper the attempt is made to estimate qualitatively the solubility, suggest the condition of the formation of continuous solid solutions with new compounds, substantiate some ideas, concerning the structure of the liquid solutions, and extend the conception. The versions on the formation of compounds in low-temperature liquid phase crystallization of solid solutions as well as the existence of the concentrated solid solutions based on aluminum and compounds are discussed.

$(IV_2)_x(III-V)_{1-x}$ type continuous solid solutions.

A number of authors obtained solid solutions of molecular elements Ge_2 and Si_2 , with some III-V type semiconductor compounds. In [2] from Ga solution-melt containing Zn continuous solid solutions of GaP and Si have been grown. We suppose that the formula of it should be $(Si_2)_x(GaP)_{1-x}$. In [3] by the method of coincident RF sputtering of GaAs and RF decomposition in Ar + SiH_4 medium on GaAs substrate at 530 – 600°C, 1 – 10 μ thick $Si_x(GaAs)_{1-x}$ epitaxial layer with Si concentration up to 55 at % were deposited. Long time annealing at 600 – 800°C has not changed the composition of the layers. The formula $Si_x(GaAs)_{1-x}$ is likely not be correct, since solubility of atomic Si in Ga and As sublattices of GaAs is less than 0,1 at %, and substituting GaAs molecule for one Si atom is hardly probable and forming only $(Si_2)_x(GaAs)_{1-x}$ is possible. The continuous solid solutions were obtained in Ge – GaAs and Ge – GaSb systems by diffusionless crystallization method [4] when 50mg drop of liquid solution was crystallized on the surface of copper cylinder rotating with rate of 8000 revs/min. However the formula of the solid solution was not suggested. J. E. Green et al. have grown from gaseous phase the solid solutions of $(Ge_2)_x(GaAs)_{1-x}$ [5] $(Ge_2)_x(GaSb)_{1-x}$ [6] in the range $0 < x < 1$. In [7,8], using a method of pyrolytic synthesis in $GeH_4 - Ga(CH_3)_3 - AsH_3 - H_2$ system $(Ge_2)_x(GaAs)_{1-x}$ epitaxial layers have been grown on GaAs (100) and Ge (100) substrates and their structures, optical and electric properties were studied. (Fig. 2)

Our results of growing variband layers of $(Ge_2)_x(GaAs)_{1-x}$ $(Si_2)_x(GaP)_{1-x}$ and $(Ge_2)_x(InP)_{1-x}$ solid solutions in the whole range of x by the method of liquid phase epitaxy were presented in [9]. Above mentioned complex semiconductors are the small part of possible cases of forming solid solutions on the basis of IV_2 and III-V materials. (Fig. 3-6)

Solubility and extended conception.

Using Boltzmann equation

$$\frac{C'_i}{C''_i} = \exp\left(-\frac{\bar{U}'_i - \bar{U}''_i}{kT}\right) \quad (1)$$

dealing with (i+1) - component two - phase system in [10] we have suggested for the solubility of i - component the following formula

$$C'_{Ni} = \frac{C''_{Ni} \exp(\Delta \bar{U}_i)}{1 + \sum_i [\exp(\Delta \bar{U}_i) - 1] C''_{Ni}} \quad (2)$$

where C'_i , C'_{Ni} , U'_i and C''_i , C''_{Ni} , U''_i are volume concentration, mole fraction and mean potential energy of i - component in (') and (') phases respectively, k - Boltzmann constant, T - absolute temperature

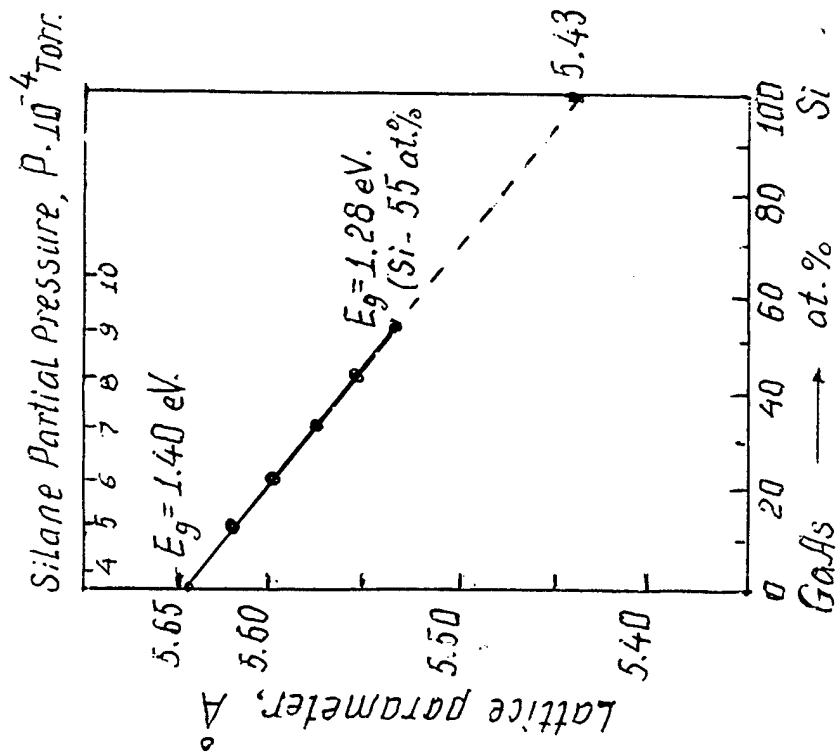


Fig. 1 Variation of lattice parameter with composition and silane partial pressure for GaAs-Si system.
 $T_s = 530 - 600^\circ\text{C}$

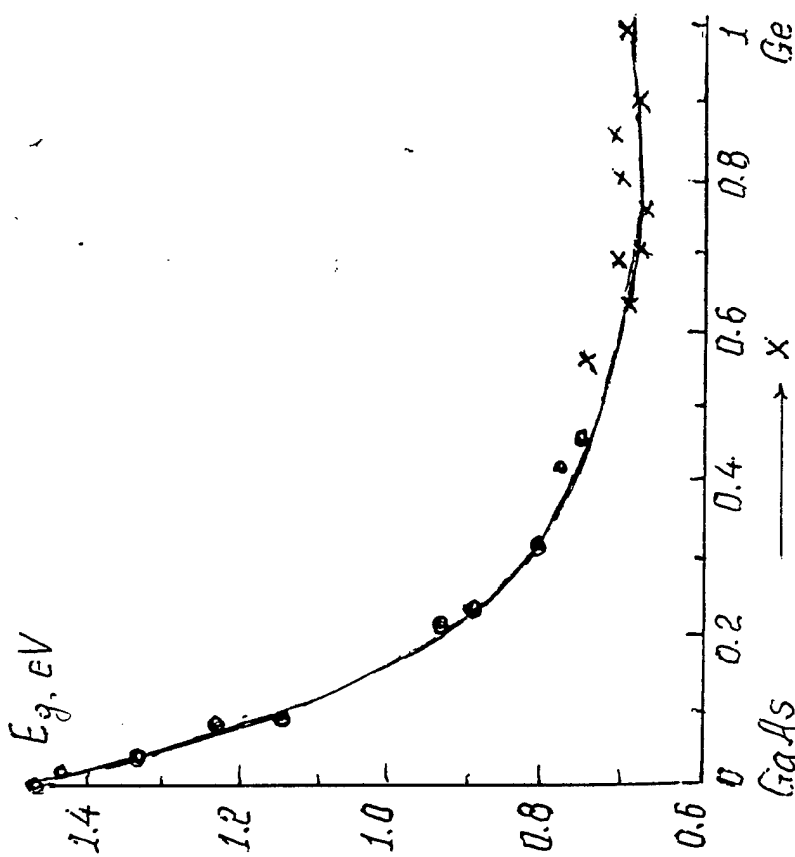


Fig. 2 • direct interband transitions
 x indirect interband transitions
 epilayers grown at 700°C
 $T_s = 600 - 800^\circ\text{C}$

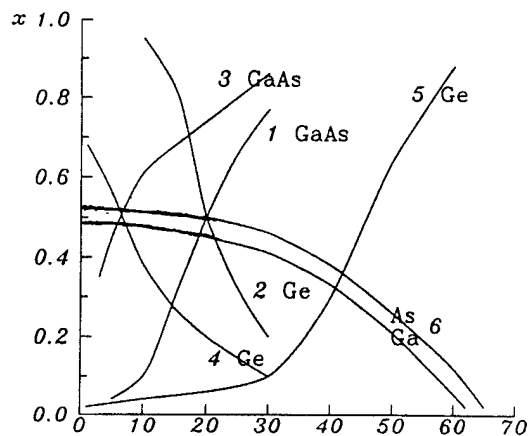


Fig. 3. Ge, GaAs, $d, \mu m$ and As distribution profiles along the thickness of $(Ge)_x(GaAs)_{1-x}$ epilayer, grown from Pb (1 - 4), Bi (5, 6) solutions on GaAs - 1, 2, 5, 6; Ge - 3, 4.

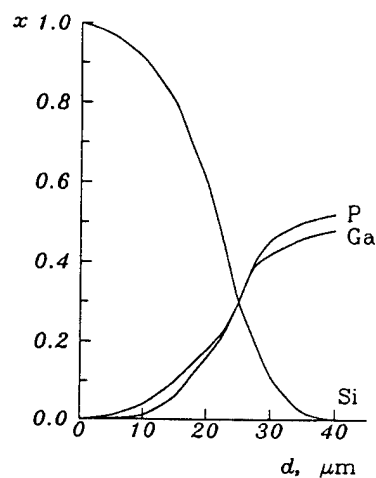


Fig. 4. Si, Ga and P distribution profiles along the thickness of $(Si_2)_x(GaP)_{1-x}$ epilayer grown on Si.

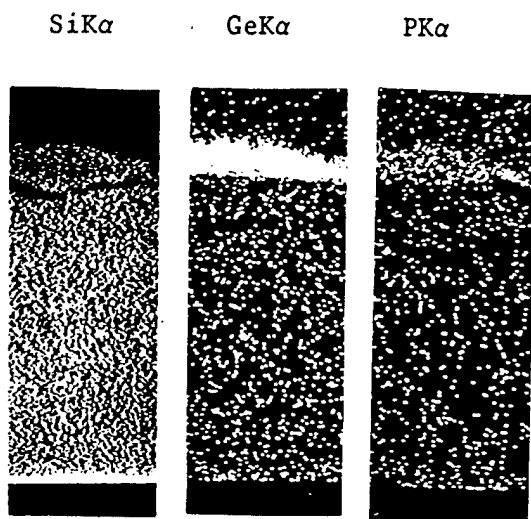


Fig. 5. Cross-section scanning electron micrographs of $Si-(GeSi)_x(InP)_{1-x}$ structure by characteristic X-rays SiKa, GeKa, PKa.

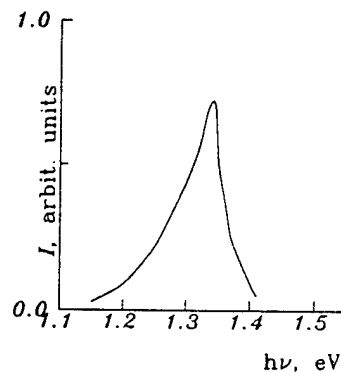


Fig. 6. Photoluminescence spectrum at 77 K from the $(GeSi)_x(InP)_{1-x}$ epilayer surface.

$$\Delta \bar{U}_i = -\frac{1}{kT} \left[(\bar{U}_i - \bar{U}_j) - (\bar{U}_i^* - \bar{U}_j^*) \right] \quad (3)$$

index j concerns the solvent. Further considering each sublattice of the ABCD type compound as a separate solvent (phase) for the solubility of the i - chemical element in the compound in [11] we have suggested

$$C'_{Ni} = C''_{Ni} \sum_{j=A}^D \frac{\exp(\Delta \bar{U}_{ij})}{1 + \sum_i [\exp(\Delta \bar{U}_{ij}) - 1] C''_{Ni}} \quad (4)$$

To predict qualitatively the behaviour of the component of solution V. K. Semenchko [12] supposed that $U = \varphi \cdot m$. φ characterizes the phase and m called by him "generalized moment" defines the particles of dissolved component. For the ion $m = ez/r$, and molecule $m = e_d/r^3$, where e is charge on electron, z is valence of the ion e_d is the dipole moment of the molecule, r is radius of the ion or molecule. According to (3) and (4) the more $|m_i - m_j|$ the less solubility of the component 1 in the solvent j and the effect of i - component on solubility of the component 1 is determined by the sign and value of $m_{i \neq 1} - m_j$. However in the case of compounds with A_2 type non-polar molecules m becomes indefinite. Thus to estimate the solubility in such systems as A_2 - BC and AB - CD (A, B, C and D are chemical elements, AB and CD are compounds) with covalent or metal bonds we suggest to use together the differences of the sum of the valences and radii of the atoms of the molecules.

$$\Delta z = z_A + z_B - (z_C + z_D) \quad (5)$$

$$\Delta r = r_A + r_B - (r_C + r_D) \quad (6)$$

As the potential energy of the interactions of the molecules of the compounds in solution depends on the number of electrons participating in interactions of the molecules and the sizes of the latters ΔU_{ij} is determined by Δz and Δr . Therefore according to (3) the more $|\Delta z|$ and $|\Delta r|$ the less the solubility and the more $|\Delta z_{ij}|$ and $|\Delta r_{ij}|$ the more the effect of the additives on solubility of the component 1. But some difficulties arise with $|\Delta z|$ when the multiplicity of the bond in A_2 or BC is not known.

Taking into account the fact that the substitutional solid solutions of metal elements [13] and binary semiconductor compounds [14] are formed in the whole range of concentrations if their components have the same type of crystal lattice, chemical compounds and difference of interatomic distances not more then 15% as well as using (5) and (6) we suggest the following condition of the formation of the continuous solutions

$$\Delta z = 0, \quad \Delta r = 2r_A - (r_B + r_C) < 0,2r_A. \quad (7)$$

On the table 1 are presented IV₂, IV-IV, III-V, II-VI and I-VII compounds, the sum of the radii of their elements and the values of Δr which satisfy (7) and

Table 1.: Values of $\Delta r = r_{IV} + r_{IV} - (r_B + r_C)$ Satisfying (7). B and C are III, II, I and V, VI, VII elements respectively.

IV ₂ , IV-IV		C ₂	Si ₂	Ge ₂	Sn ₂	GeC	SnC	SiGe	SiSn	GeSn
B - C	$r_{IV} + r_{IV}$ $r_B + r_C$	1.54	2.34	2.44	2.80	1.99	2.17	2.39	2.57	2.62
BN	1.58	-0.04	-	-	-	-	-	-	-	-
AlN	1.96	-	-	-	-	0.03	0.21	-	-	-
GaN	1.96	-	-	-	-	0.03	0.21	-	-	-
InN	2.14	-	0.20	-	-	-0.15	0.03	0.25	-	-
BP	1.98	-	-	-	-	-	0.19	-	-	-
AlP	2.36	-	-0.02	0.08	-	-	-0.19	0.03	0.21	0.26
GaP	2.36	-	-0.02	0.08	-	-	-0.19	0.03	0.21	0.26
InP	2.54	-	-0.20	0.10	-	-	-	-0.15	0.03	0.08
BAs	2.06	-	-	-	-	-0.07	0.11	-	-	-
AlAs	2.44	-	-0.10	0.00	-	-	-	-0.05	0.13	0.18
GaAs	2.44	-	-0.10	0.00	-	-	-	-0.05	0.13	0.18
InAs	2.60	-	-	-0.18	0.18	-	-	-0.23	-0.05	0.00
BSb	2.24	-	-0.10	0.20	-	-	-0.07	0.15	-	-
AlSb	2.62	-	-0.29	-0.18	0.18	-	-	-0.23	-0.05	0.00
GaSb	2.62	-	-0.28	-0.19	0.18	-	-	-0.23	-0.05	0.00
InSb	2.80	-	-	0.36	0.00	-	-	-	-0.23	-0.28
BeO	1.76	-0.22	-	-	-	-	-	-	-	-
ZnO	1.97	-	-	-	-	0.02	0.20	-	-	-
ZnS	2.35	-	-0.01	0.09	-	-	-0.18	0.04	0.22	0.27
ZnSe	2.45	-	-0.11	-0.01	-	-	-	-0.06	0.12	0.17
ZnTe	2.63	-	-0.29	-0.19	0.17	-	-	-0.24	-0.06	-0.01
CdS	2.52	-	-0.18	-0.08	0.28	-	-	-0.13	0.05	0.10
CdSe	2.62	-	-0.28	-0.18	0.18	-	-	-0.23	-0.05	0.00
CdTe	2.80	-	-	0.36	0.00	-	-	-	-0.23	-0.18
HgS	2.52	-	-0.18	-0.08	0.28	-	-	-0.13	0.05	0.10
HgSe	2.62	-	-0.28	-0.18	0.18	-	-	-0.23	-0.05	0.00
HgTe	2.80	-	-	-0.36	0.00	-	-	-	-0.23	-0.18
CuF	1.98	-	-	-	-	0.01	0.19	-	-	-
CuCl	2.33	-	0.01	0.11	-	-	-0.16	0.06	0.24	-
CuBr	2.45	-	-0.11	0.11	-	-	-0.28	-0.06	0.12	0.17
CuI	2.62	-	-0.28	-0.18	-0.18	-	-	-0.23	-0.05	0.00
LiF	2.16	-	0.18	0.28	-	-0.17	0.01	0.23	-	-
LiCl	2.51	-	-0.17	-0.07	0.29	-	-	-0.12	0.06	0.11
LiBr	2.63	-	-	-0.19	0.17	-	-	-0.24	-0.06	-0.01
LiI	2.80	-	-	-	0.00	-	-	-	-0.23	-0.18
NaF	2.50	-	-0.16	-0.06	-	-	-	-0.11	0.07	0.12
NaCl	2.85	-	-	-	-0.05	-	-	-	-	-0.23
NaBr	2.97	-	-	-	-0.17	-	-	-	-	-0.33
NaI	3.14	-	-	-	-0.34	-	-	-	-	-

shows the possibility of the formation of the continuous solid solutions with new chemical compounds.

Consider the crystallization of substitutional solid solution of A with BC from liquid metal solvent S at the temperatures lower than the melting point of A and BC(B,C). The compound BC can also be dissociated in liquid phase. In forming the solid solution $(BC)_{1-x}(A_2)_x$ with $0 < x < 0,5$ (BC is solid solvent) A_2 substitutes BC and formation of $(A_2)_{1-x}(BC)_x$ takes place as a result of substitution of A_2 by BC which can also originate with crystallization.

A success of the experiments on growth of the solid solutions depends on the choice of all components A, BC (B, C) and S when the solubility of A and BC in S should be enough to provide the deposition rate required. In some cases to increase the solubility of A in S one should find the suitable additive to introduce into liquid solution. To this end one needs to carry out an additional experiment or use some new idea on the formation of solutions. It is not excluded that in introducing the additive D into S the solubility of A increases as a result of the formation of the compound AD the molecules of which substitute the pair of atoms (molecules) S_2 ($2S$) of the liquid solvent. So we suppose that there also exist substitutional and interstitial liquid solutions. To back up this idea we note such facts: 1. The solid and liquid substances are incompressible. 2. There is the short-range order in liquids. 3. The difference of binding energy of the elements in solid and liquid states is within 3-10%, since their heat of sublimation is 10-40 times as large as the heat of melting [15]. In this context we suggest the following extended conception. In the multicomponent systems the formation of the concentrated liquid or solid solutions is possible as a result of origination and dissolution of new chemical compounds, which are not shown on the traditional phase diagrams.

Versions on the formation of new compounds.

1. Initial phase the solution of A and BC in liquid (L) metal solvent S is at temperature close to melting (L) point of A $T_{L,A} < T_{L,BC}$. Atom (mole) fraction of $C_{N,S}^L > C_{N,BC}^L$, $C_{N,A}^L$ and $C_{N,BC}^L > C_{N,A}^L$. In cooling to some reaction (r) temperature T_r when binding energy between A atoms $E_{AA} \geq 3/2kT_r$ the reaction $A+A \leftrightarrow A_2$ takes place. In further cooling to the crystallization (c) temperature $T_{c,BC}$ when liquid phase is saturated by the compound BC solid solution $(BC)_{1-x}(A_2)_x$ is deposited. (cooling version). If $C_{N,A}^L > C_{N,BC}^L$ and liquid solution is cooled to $T_{c,A}$ when it is saturated by A $(A_2)_{1-x}(BC)_x$ crystals will be obtained.
2. Both Maxwell-Boltzmann and Gibbs distribution laws show that there are in the system considered above molecules A_2 with the life time τ . At saturating the liquid phase by A the concentration of A_2 increases. If the deposition time of A_2 from liquid phase-crystal boundary layer on the crystal $\tau_d < \tau$ $(BC)_{1-x}(A_2)_x$ solid solution is formed (statistical version). $(A_2)_{1-x}(BC)_x$ solid solution with $0 < x < 0,5$ (A_2 is solid solvent) is formed according to the versions described when compound BC is dissociated in the liquid phase.
3. All other things being equal an adsorption of molecule A_2 is more than that of atom A, since in forming the molecule A_2 the intensity of the field of A decreases.

In addition an adsorption is known to increase with a reduction in temperature. As the adsorption takes place to decrease the energy of surface it acts as the catalyst of the reaction $A + A \leftrightarrow A_2$ (fig.1.a), which leads to the formation of solid solution $(BC)_{1-x}(A_2)_x$ (fig.1c), (adsorption version). Similarly $(A_2)_{1-x}(BC)_x$ is formed when BC is dissociated in S (fig.1 b,d). In figures two-dimensional phases are described. 4. As a rule the solubility of the monoatomic A in the crystal BC and B and C in the crystal of A is less than 1 at % and dissolution deforms a lattice and induces the strain in it. In fig.2a the deposition of monoatomic layer of solid solution of BC saturated by A on BC substrate is presented. In fig. 2. the liquid phase is not shown. The pairing of A atoms in the previous layer decreases the lattice strain and causes an increase of concentration of A in the growing layer (fig.2c) and the formation of $(BC)_{1-x}(A_2)_x$ solid solution (fig. 2e). As the pairing of A atoms normalizes lattice parameter of BC crystal we call this pseudomorphism version. Similarly $(A_2)_{1-x}(BC)_x$ is formed when BC is dissociated in liquid phase (fig 2b,d,f). The formation of solid solutions according to the versions 2-4 can occur at the same time.

Possible aluminium concentrated solid solutions

Aluminium alloys are of special importance for flying vehicles and a lot of other applications. In order to predict some possible cases of the formation of aluminium continuous solid solutions with new chemical compounds, on the basis of above suggested conception and the condition (7) we have considered phase diagrams of the aluminium and different binary systems [16] compared valencies metal and covalent radii of the majority of elements. On the table 2 are presented some of the possible new chemical compounds sum of the radii (upper numbers are metal and lower ones are covalent) of their components and values of Δr , which satisfy (7), and hence the formation of $(Al_2)_{1-x}(BC)_x$ solid solutions with $0 < x < 1$ can be expected. Note, that Ti, Mn, Fe, Co and Ni are not elements of II group, but in some cases they show divalence. There are CoSn, FeSn, and SiTi compounds on the phase diagrams of the binary systems Co-Sn, Fe-Sn and Si-Ti respectively. Sn, Bi and Pb seem to be the suitable liquid metal solvents.

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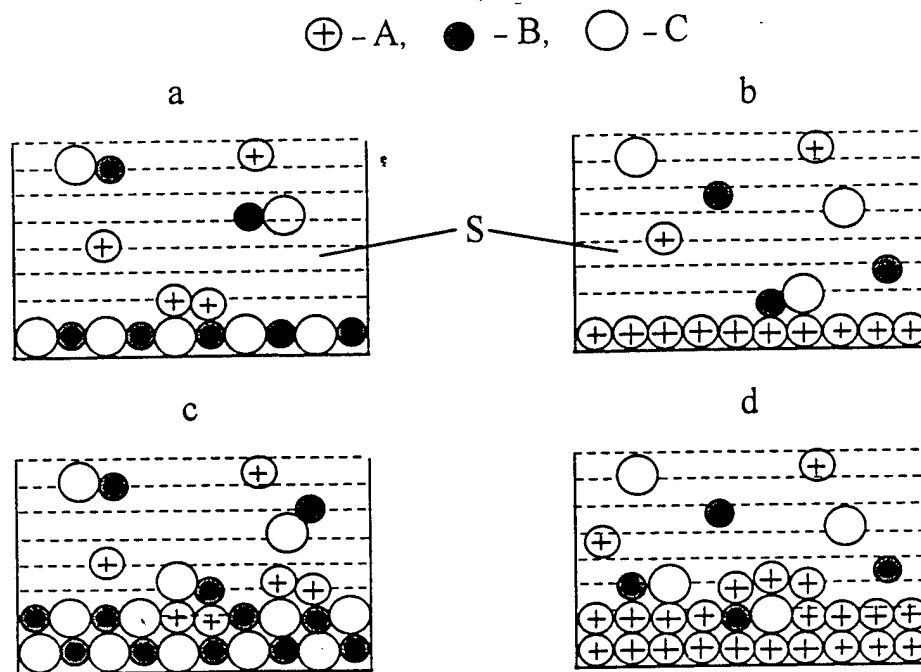


Fig.1. Pairing of A on the surface of BC crystal (a) B with C on A substrate (b) and formation of $(BC)_{1-x}(A_2)_x$ (c), $(A_2)_{1-x}(BC)_x$ (d) solid solutions.

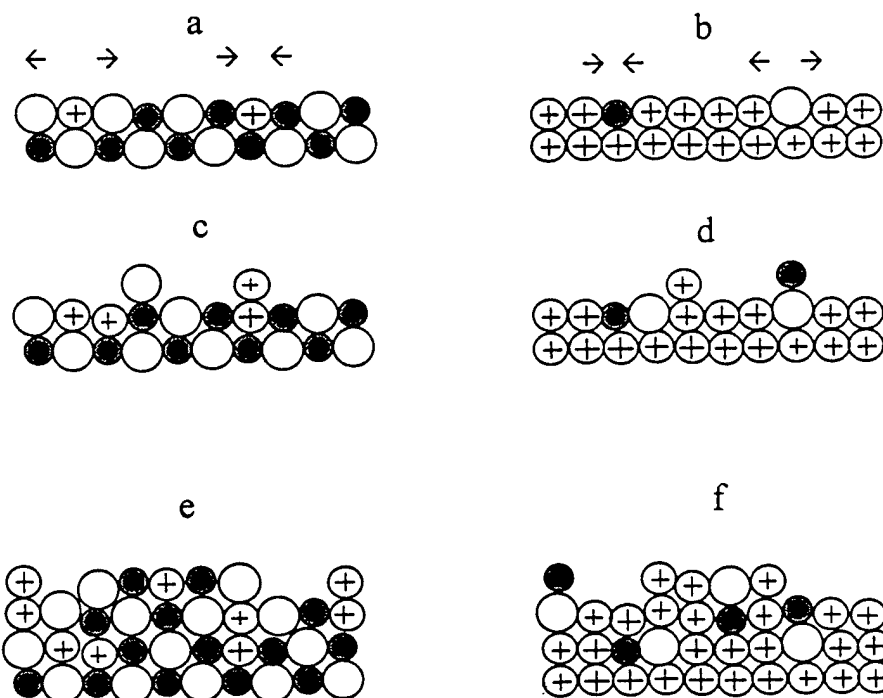


Fig.2. Dissolution of A in BC (a) B and C in A (b) pairing of A in BC (c) B with C in A (d) and formation of $(BC)_{1-x}(A_2)_x$ (e), $(A_2)_{1-x}(BC)_x$ (f) solid solutions.

Table 2.: Compounds forming $(Al_2)_{1-x}(BC)_x$ continuous solid solutions

$2r_{Al,m}=2.86\text{\AA}$, $2r_{Al,c}=2.52\text{\AA}$
 indices: m-metal, c-covalent

BC type compound supposed	r_B+r_C , Å	Δr , Å	BC type compound supposed	r_B+r_C , Å	Δr , Å
CuSb	2.89	-0.03	ZnPb	3.11	-0.25
	2.53	-0.01		2.77	-0.25
CuBi	3.10	-0.24	CdSi	2.86	0.00
	2.63	-0.11		2.65	-0.13
BeGe	2.52	0.34	CdGe	2.91	-0.05
	2.29	0.23		2.70	-0.18
BeSn	2.71	0.15	CdSn	3.10	-0.24
	2.47	0.05		2.88	-0.36
BePb	2.87	-0.01	HgSi	2.89	-0.03
	2.53	-0.01		2.65	-0.13
MgSi	2.94	-0.08	HgGe	2.94	-0.08
	2.57	-0.05		2.70	-0.18
MgGe	2.99	-0.13	TiSi	2.79	0.05
	2.62	-0.10		2.49	0.03
MgSn	3.18	-0.32	TiGe	2.94	-0.08
	2.80	-0.28		2.54	-0.02
CaC	2.83	0.03	MnSn	2.89	-0.03
	2.51	0.01		2.57	-0.05
ZnSi	2.71	0.15	FeSn	2.85	0.01
	2.48	0.04		2.57	-0.05
ZnGe	2.76	0.10	CoSn	2.84	0.02
	2.53	-0.01		2.56	-0.04
ZnSn	2.95	-0.09	NiSn	2.82	0.04
	2.71	-0.19		2.55	-0.03

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